Highlights from recent literature

1 Analytical

1.1 Method for measuring impurity elements in high-purity gold with small-size extraction apparatus

Inventors Y Li, Q Hu, Z Huang, X Yang, Q Wei, G Yang, Y Huang from the Yuxi Normal University, Peop. Rep. China, Patent No CN 101285744, A, October 2008 The title application comprises a cannula, and a seperating pistol with capillary at the center. The title method comprises the steps of: treating a sample with microwave, separating Au matrix by microextraction with the micro extraction application, optimizing working parameters of instruments, choosing isotopes and internal std., correcting the interference of common ion effect, performing half-quant. scanning, preparing a ref. solution, measuring with plasma mass spectrum, and calculating to obtain result. The inventive app. has a 1-time extn. rate of 98% and a recycling rate of impurities of 95%. The inventive method eliminates the interference of Au of the measurement onto impurity elements with ICP-MS (inductively coupled plasma mass spectrometry) method, and as a trace anal. method, it has high sensitivity, low detection limit, small sample consumption, and high speed.

2 Catalysis

2.1 Nanoscale gold supported manganese oxide/iron oxide catalyst, and preparation method and application thereof

The title catalyst comprises manganese oxide and iron oxide as carrier and gold nanoparticle supported thereon. Y Chen, M Lin, H Hsu, J Lin, Patent No. CN 101284239, A, October 2008 The application for removing CO in gas comprises oxidizing CO in reactive gas containing O_2, CO, H_2 and He in the presence of the above catalyst into carbon dioxide in a continuous packed bed reactor. The invention may avoid CO poisoning of fuel cell electrode.

2.2 Interaction between metallic gold and support and its influence on catalysis

The interaction between gold particles and support in Au/TiO_2 and Au/Al_2O_3 catalysts prepared by immobilizing colloidal gold on the support was evidenced by XPS. X Yang, Y Shen, D Wang, Y Sun, Yongan from the College of Chemistry and Chemical Engineering, the Inner Mongolia, University, Huhhot, 010021, Peoples Rep. China, *Reaction Kinetics and Catalysis Letters*, 2008, **95(1)**, 123. The reducibility of the support is more responsible than the interaction between the nanogold particles and support for the activity of catalysts.

2.3 Selective oxidation with dioxygen by gold nanoparticle catalysts derived from 55-atom clusters

Supported gold nanoparticles have excited much interest owing to their unusual and somewhat unexpected catalytic properties, but the origin of the catalytic activity is still not fully understood. M Turner V Golovko, O Vaughan, P Abdulkin, A Berenguer-Murcia, M Tikhov, B Johnson, R Lambert, from the Department of Chemistry, University of Cambridge, Cambridge, *Nature (London, United Kingdom)*,2008, **454**(7207), 981.

Experimental work on gold particles supported on a titanium dioxide (110) single-crystal surface has established a striking size threshold effect associated with a metal-to-insulator transition, with gold particles catalytically active only if their diameters fall below .apprx.3.5 nm. However, the remarkable catalytic behaviour might also in part arise from strong electronic interaction between the gold and the titanium dioxide support. In the case of industrially important selective oxidation reactions, explanation of the effectiveness of gold nanoparticle catalysts is complicated by the need for additives to drive the reaction, and/or the presence of strong support interactions and incomplete understanding of their possible catalytic role. Here we show that very small gold entities (.apprx.1.4 nm) derived from 55-atom gold clusters and supported on inert materials are efficient and robust catalysts for the selective oxidation of styrene by dioxygen. We find a sharp size threshold in catalytic activity, in that particles with diameters of .apprx.2 nm and above are completely inactive. Our observations suggest that catalytic activity arises from the altered electronic structure intrinsic to small gold nanoparticles, and that the use of 55-atom gold clusters may prove a viable route to the synthesis of robust gold catalysts suited to practical application.

2.4 Identification of active gold nanoclusters on iron oxide supports for CO oxidation

Gold nanocrystals absorbed on metal oxides have exceptional properties in oxidation catalysis, including the oxidation of carbon monoxide at ambient temps., but the identification of the active catalytic gold species among the many present on real catalysts is challenging. A Herzing, C Kiely, A Carley, P Landon, G Hutchings from the Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA, USA, *Science* (*Washington, DC, United States*) 2008, **321**(5894), 1331. The authors have used aberration-cor. scanning transmission electron microscopy to analyze several iron oxide-supported catalyst samples, ranging from those with little or no activity to others with high activities. High catalytic activity for carbon monoxide oxidation is correlated with

the presence of bilayer clusters that are ~0.5 nm in diameter and contain only ~10 gold atoms. The activity of these bilayer clusters is consistent with that demonstrated previously with the use of model catalyst systems.

2.5 Catalytically active gold on ordered titania supports

A review is presented, which summarizes the current understanding of the origin of the unique properties of titania-supported Au catalysts for carbon monoxide oxidation M Chen, W Goodman from the Department of Chemistry, Texas A&M University, College Station, TX, USA, *Chemical Society Reviews* 2008, **37(9)**, 1860. The key issues of catalysis by nanostructured Au, effects of oxide support and active site/structure, esp. those provided from model studies are discussed in detail. The successful synthesis of a highly catalytically active gold bilayer may lead to the design and synthesis of practically active Au nanofilm catalysts.

2.6 Selective oxidation using gold

A review. This critical review covers recent developments in catalytic studies of gold in selective oxidation of organic compds. C Della Pina, E Falletta, L Prati, M Rossi, Michele from the Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita degli Studi di Milano, Milan, Italy, *Chemical Society Reviews* 2008, **37(9)**, 2077. The unique, outstanding properties of Au nanoparticles, a biocompatible non-toxic metal, have allowed the development of stable and selective catalysts for conversion of many organic feedstocks to valuable chemicals. A critical discussion of results of different research groups is presented along with attempts to correlate the catalytic properties with catalyst morphology in non-equiv. series of experiments. Efforts towards optimized synthesis of products of industrial appeal such as propylene oxide, vinyl acetate monomer, cyclohexanol/cyclohexanone, gluconic acid, and glyceric acid are outlined.

2.7 Preparation and structural characterization by XRD and XAS of the supported gold catalysts

A series of supported gold catalysts were studied by X-ray diffraction (XRD) in order to determine the Au average particle size, microstrain information and probability of faults. M Lazar, V Almasan, S Pintea, B Barz, C Ducu, V Malinovschi, X Yaning, N Aldea from the National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania, *Journal of Optoelectronics and Advanced Materials* 2008, **10(9)**, 2244.

The gold catalysts samples (up to 5 wt.% gold content) were prepared by two methods - impregnation of the oxidic support with aq. solution of $HAuCl_4.3H_2O$ and homogeneous deposition-precipitation using urea as precipitating agent. The following metal oxides, with high specific surface area were used as supports: Cr_2O_3, CeO_2, TiO_2, SiO_2, Al_2O_3 and ZrO_2. The XRD method is based on the deconvolution of the Experimental X-ray line profiles (XRLP) (111), (200), (220) and (311) using Fourier transform procedure. The global structure is detd. by fitting the XRLP with the generalized Fermi function. The X-ray diffraction data was collected at room temp, using Bragg-Brentano (BB) geometry installed on DRON 2 set up, connected with a PC. The samples were next analyzed by extended X-ray absorption fine structure (EXAFS) of the Au LIII-edge using synchrotron radiation in order to determine their local structure that explains the strong deformation of the metal due to its interaction with the oxide supports.

2.8 H_2-Induced promotion of CO oxidation over unsupported gold

The kinetics and mechanism of the preferential oxidation of carbon monoxide in the presence of hydrogen (PrOx) over an unsupported gold powder (mean particle size.apprx.20 nm and free of silver) have been investigated using flow fixed-bed catalytic testing and diffuse reflectance IR Fourier transform spectroscopy coupled to mass spectrometry (operando DRIFTS or DRIFTS-MS). E Quinet, L Piccolo, H Daly, F Meunier, F Morfin, A Valcarcel, F Diehl, P Avenier, V Caps, J-L; Rousset, Institut de recherches sur la catalyse et l'environnement de Lyon, (IRCELYON, UMR 5256 CNRS/University of Lyon), Villeurbanne, France, *Catalysis Today*, 2008, **138(1-2)**, 43. It is shown that the presence of H_2 has a favorable effect on the oxidation of CO, either by strongly accelerating the reaction or by preventing the catalyst deactivation, depending on the conditions used. Variation of the hydrogen partial pressure has allowed us to determine partial reaction orders for both CO oxidation and H_2 oxidation under PrOx conditions. An IR band at .apprx.2113 cm-1, corresponding to on-top CO adsorption on metallic gold, has been obsd. below 150. degree. In addition, adsorbed hydroxyl groups gradually develop simultaneously to gas-phase water in the course of the reaction at increasing temps. The promotional effect of hydrogen is ascribed to highly oxidative HxOy intermediates formed from the interaction between H_2 and O_2 on the gold surface.

2.9 Supported gold and gold palladium catalysts for selective chemical synthesis

A review. Catalysts based on gold are now well established as very active and selective for broad ranges of redox reactions. G Hutchings from the School of Chemistry, Cardiff University, Cardiff, UK, *Catalysis Today*, 2008, **138(1-2)**, 9. Although primarily known for selective and preferential oxidation reactions, gold catalysts are also highly effective for selective hydrogenation. In this article, two hydrogenation reactions are discussed; namely, the use of supported gold catalysts for selective hydrogenation of alpha, beta, -unsaturated aldehydes to unsaturated alcohols, and the use of supported gold palladium alloys for the direct hydrogenation of molecular oxygen to form hydrogen peroxide in preference to water.

2.10 Way to distribute and fix gold fine particles on a support, gold fine particle-containing support, catalyst, and colorant

The invention refers to a method of distributing and fixing gold particles on a support, wherein a sublimable gold precursor (di-Me Au acetylacetonate, di-Me Au trifluoro acetylacetonate, chloro tri methylphosphine Au complex, Me(tri methylphosphine) Au complex, etc.) and an inorganic or organic support (polymer, inorganic oxide, active C, porous metal complex) is mixed together as solids while applying mech. friction at room temp. and normal pressure, and then reduced. M Haruta, G Ishida, I Okuda, K Kuroda, N Kinoshita, S Suenaga, Y Yamaguchi, from the Tokyo Metropolitan University, Japan, Patent No, JP 2008259993, A, Oct 2008. The Au nanoparticles or metal cluster supporting body thus obtained is used as catalyst for the oxidation of glucose to gluconic acid, and as a colorant.

2.11 Theory and simulation in heterogeneous gold catalysis

This critical review covers the application of quantum chem. to the burgeoning area of the heterogeneous oxidation by Au. R Coquet, K Howard, D Willock, from the Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK, *Chemical Society Reviews*, 2008, **37(9)**, 2046. We focus on the most established reaction, the oxidation of CO at low temp. The review begins with an overview of the methods available comparing the treatment of the electron-electron interaction and relativistic effects. The structure of Au particles and their interaction with oxide reviews is then discussed in detail. Calculations of the adsorption and reaction of CO and O_2 are then considered and results from isolated and supported Au clusters compared (155 refs.).

2.12 Supported gold nanoparticles as catalysts for organic reactions

A review. This critical review is intended to attract the interest of organic chemists and researchers on green and sustainable chem. on the catalytic activity of supported gold nanoparticles in organic transformations. A Corma, H Garcia, from the Instituto de Tecnologia Quimica CSIC-UPV, Universidad Politecnica de Valencia, Valencia, Spain, *Chemical Society Reviews*, 2008, **37(9)**, 2096. In the general part of this crit. review, emphasis is given to the different procedures to form supported gold nanoparticles and to the importance of the support cooperating in the catalysis. Also the convergence of homogeneous and heterogeneous catalysis in the study of gold nanoparticles has been discussed. The core part of this review is constituted by sections in which the reactions catalyzed by supported gold nanoparticles are described. Special emphasis is made on the unique ability of gold catalysts to promote additions. to multiple C-C bonds, benzannulations, and alc. oxidation by oxygen.

2.13 Enhanced carbon monoxide oxidation activity over gold-ceria nanocomposites

The composites with nanosized gold loaded in nanoporous ceria were prepared on a large scale by a facial and environment-benign sol-gel process. Z Chen, Q Gao, State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, Peop. Rep. China, *Applied Catalysis, B: Environmental*, 2008, **84(3-4)**, 790. These materials were characterized by XRD, ICP, BET, UV-vis absorption, XPS, HRTEM and EDX. The main factors such as size and surface state of the Au and defect in the ceria could be adjusted by acid treatment of the composites in ascorbic acid solution to improve the activity and decrease the content of noble metal Au in the materials. Enhanced catalytic activities were obtained for the CO oxidation reaction over the catalysts due to the small crystal sizes with narrow size distributions of gold nanoparticles, a large amt. of defects in the nanoporous ceria support, as well as a high ratio of Au^{3+}/Au0 in the nanocomposites.

2.14 Gold supported on mesoporous titania thin films for application in microstructured reactors in low-temperature water-gas shift reaction

Au (1 wt.%)/TiO_2 catalytic thin films were prepared on a surface-modified titanium substrate for application in a water-gas shift (WGS) microstructured reactor. Au- containing mesoporous titania films were synthesized using Pluronic 127 surfactant as a structure directing agent and titanium tetrabutoxide as titania source. Colloidal gold nanoparticles of 4 nm diameter were added to the synthesis sol prior to spin-coating. E Rebrov, A Berenguer-Murcia, B Johnson, J Schouten, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands, *Catalysis Today* 2008, **138(3-4)**, 210. The resulting thin films were characterized by X-ray diffraction, transmission electron microscopy, ethanol adsorption-desorption isotherms and spectroscopic ellipsometry. Catalytic activity and selectivity were measured for the WGS reaction at temps. between 220 and 290. degree.C. The reaction rate measured at CO conversions of below 10% was similar to that reported for gold supported on mesoporous titania and on ceria modified mesoporous titania pelletized catalysts prepared via deposition-precipitation.

2.15 Gold supported on La_2O_3: structure and reactivity with CO_2 and implications for CO oxidation catalysis

A sample consisting of Au dispersed on high-area porous La_2O_3 was prepared by adsorption of dimethylgold acetylacetonate. M Mihaylov, E Ivanova, Y Hao, K Hadjiivanov, H Knoezinger, B Gates, Department Chemie and Biochemie, Physikalische Chemie, LMU Muenchen, Germany, *Journal of*

Physical Chemistry C 2008, **112(48)**, 18973. X-ray absorption and IR spectroscopies characterized the Au species and their ligands, and CO as a probe mol. was used with IR spectroscopy to follow changes in Au species under various reaction conditions, focusing on oxidn.-redn. processes. Au on the initially prepared sample was present as Au^{3+} species; however, only a small fraction was apparently reactive with the CO probe mol.

After evacuation at elevated temps, the Au was first reduced yielding clusters incorporating pos.-charged Au species, which in turn were converted to neutral Au species. CO and O_2 reacted with the reduced sample in a process which appeared to be auto-catalytic and related to the existence of oxidized Au species which facilitate O_2 activation and CO oxidation catalysis. Surprisingly, it was established that although they are inert toward O_2 at room temp, the supported Au nano-particles were readily oxidized by CO_2, a result which suggested CO_2 may be the actual oxidant of Au in CO oxidation catalysis. Supported zero-valent Au nano-particles were also easily oxidized by NO and NO_2.

2.16 Palladium and gold-palladium catalysts for the direct synthesis of hydrogen peroxide

A review; today hydrogen peroxide is produced by an indirect process in which an alkyl anthraquinone is sequentially hydrogenated and oxidized. In this way hydrogen and oxygen are kept sep. during the manufg. process. J Edwards, G Hutchings, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK, *Angewandte Chemie, International Edition* 2008, **47(48)**, 9192. A process where mol. oxygen is directly hydrogenated could be preferred if control of the sequential hydrogenation can be achieved, particularly if high rates can be attained under intrinsically safe, non-explosive conditions. Herein we describe recent progress in the direct synthesis of hydrogen peroxide using supported palladium and gold-palladium alloy catalysts and consider some of the problems that have to be overcome.

3 Chemistry

3.1 Characterization of silicate glasses doped with gold by solid-state field-assisted ion exchange

The doping of silicate glasses with transition metals (with the possibility to induce the formation of metallic nanoparticles by suitable post-exchange treatments) attracts a great attention for its potential in light waveguides technol., ultrafast nonlinear optics, luminescent and magnetic materials. E Cattaruzza, G Battaglin, F Gonella, S Ali, C Sada, A Quaranta, Department of Physical Chemistry, Universita Ca' Foscari Venezia, Venice, Italy, *Materials Science & Engineering, B: Advanced Functional Solid-State Materials* 2008, **149(2)**, 195. Moreover, the control of the metal distribution inside the glass is a central issue for both the understanding of the incorporation process and for the definition of useful precipitation protocols. In the presented experimental, gold-containing silicate glasses were prepared by solid-state field-assisted ion exchange. A metallic film of gold was deposited onto two different glass substrates by sputtering. Then, the substrates were heat-treated under intense elec. field to induce diffusion of gold inside the glass network. Structural and compositional characterizations were performed by different techniques: secondary ion mass and Rutherford backscattering spectrometries, and optical absorption spectroscopy.

3.2 Synthesis of 28-membered macrocyclic polyammonium cations functionalized gold nanoparticles and their potential for sensing nucleotides

A new synthesis of underivatized gold nanoparticles (Au-NPs) in water stabilized by the highly water sol. 28-membered macrocyclic polyammonium chloride, [28]ane-$(NH^{2+})_6O_2$.6Cl- (28-MCPAC) is reported. T Misra, C Liu, Department of Chemistry, National Taiwan University, Taipei, Taiwan, *Journal of Colloid and Interface Science* 2008, **326(2)**, 411. In addition. to providing stability, 28-MCPAC with its cationic form functionalizes the Au-NPs for sensing anions in water. The 28-MCPAC-Au-NPs show a surface plasmon band in the visible region (>520 nm). By tuning the 28-MCPAC:HAuCl4 ratio, Au-NPs with different core diameters ranging from 4 nm to 6 nm, as detected by TEM anal., can be obtained. Particles are spherical, discrete, and appeared to have narrow size distributions. Raman spectroscopy confirms that the physisorption is responsible for the interaction between Au-NP surface and 28-MCPAC. The potential of the as-synthesized particles for sensing monophosphorylated nucleosides (nucleotides): 5-adenosine monophosphate (5-AMP), 5-cytosine monophosphate (5-CMP), 5-guanine monophosphate (5-GMP), and 5-uridine monophosphate (5-UMP) is investigated spectroscopically. Nucleotides-assisted agglomerations of 28-MCPAC-Au-NPs follow the order: 5-UMP > 5-GMP > 5-CMP > 5-AMP. An attempt is taken to prepare Au-NPs in water at pH 4.55 without an added stabilizer. Particles without an added stabilizer are short lived, and the TEM image shows that the particles aggregate following a quasi-two-dimensional self-assembly array.

3.3 Chalcogenide centered gold complexes

A review. Chalcogenide-centered gold complexes are an important class of compds. in which a central chalcogen is surrounded by several Au atoms or Au and other metals. M Gimeno, A Laguna, Departamento de Quimica Inorganica, Instituto de Ciencia de Materiales de Aragon, CSIC, Universidad de Zaragoza, Zaragoza, Spain, *Chemical Society Reviews* 2008, **37(9)**, 1952. They have special characteristics such as unusual geometries, electron deficiency, and properties such as luminescence or nonlinear optical properties. The best

known species are the trinuclear [E(AuPR3)3]+, oxonium' type species, that have high synthetic applicability, not only in other chalcogen-centered species, but in many other organometallic derivs. The aurophilic interactions play an important role in the stability, preference for a particular geometry and luminescence properties in this type of derivs.

4 Electrochemistry

4.1 Electrochemical determination of nitrite and Iodate by use of gold nanoparticles/ poly(3-methylthiophene) composites coated glassy carbon electrode

A promising electrochem. sensor was fabricated by electrodeposition of gold nanoparticles on poly (3-methylthiophene) (P3MT)-modified glassy carbon electrode (GCE), forming a nano-Au/P3MT composites-modified GCE (nano-Au/P3MT/GCE). X Huang, Y Li, Y Chen, L Wang, Anhui Key Laboratory of Chemo-Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Peop. Rep. China, *Sensors and Actuators, B: Chemical* 2008, **B134(2)**, 780. Field emission scanning electron microscope (FE-SEM) and electrochem. techniques were used for the characterization of these composites. Nano-Au/P3MT layer was very uniform, and formed a kind of nanoporous structure.

Electrochem. experiments showed that this proposed nano-Au/P3MT composites-modified electrode exhibited excellent electrocatalytic properties for NO_2- and IO_3-. Amperometry revealed that there existed a good linear relationship between peak current with the concn. in the range of 10-1000 .mu.M and the detection limit of 2.3.mu.M for NO_2. and in the range of 5-500 .mu.M and the detection limit of 1.4 .mu.M for IO_3-. The proposed method was used as an amperometric detector for anal. of NO_2- and IO_3- in iodized table salt and results were satisfactory. The nano-Au/P3MT composites-modified electrode had good storage stability, reproducibility and anti-interference ability for promising practical application.

4.2 Electronic and transport properties of contacts between molybdenum sulfide nanowires and gold electrodes

We report unique electronic and transport properties of contacts between a molybdenum sulfide nanowire and a gold electrode. I Popov, A Pecchia, S Okano, N Ranjan, A Di Carlo, G Seifert, Gotthard, Institut fuer Physikalische Chemie, Technische Universitaet Dresden, Dresden, Germany, *Applied Physics Letters* 2008, **93(8)**, 083115/1. The point-like contacts exhibit a remarkable transparency for the charge carrier injection, which is the consequence of the "task division" between sulfur and molybdenum atoms at the interface with the gold electrode, where sulfur binds the nanowire to the electrode, and the current flows unperturbed through the direct Au-Mo channels. The unique properties of the analyzed contacts solve some major drawbacks in the mol. electronics devices, such as the difficulties for the current injection from the electrodes into conjugated carbon-based mols. (c) 2008 American Institute of Physics.

5 Electronics and sensors

5.1 A novel nonenzymatic hydrogen peroxide sensor based on a polypyrrole nanowire-copper nanocomposite modified gold electrode

A novel nonenzymic H_2O_2 sensor was fabricated by dispersing copper nanoparticles onto polypyrrole (PPy) nanowires by cyclic voltammetry (CV) to form PPy-copper nanocomposites on gold electrodes. SEM was used to characterize the morphologies of the PPy nanowires and the PPy-copper nanocomposite. T Zhang, R Yuan, Y Chai, W Li, S Ling, Chongqing Key Laboratory of Analytical Chemistry, College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, Peop. Rep. China, *Sensors* 2008, **8(8)**, 5141. The reactivity of the PPy-copper nanocomposite towards H_2O_2 was characterized by cyclic voltammetry and chronoamperometry. Effects of applied potential, the concns. of detection solution upon the response currents of the sensor were investigated for an optimum anal. performance. It was proved that the PPy-copper nanocomposite showed excellent catalytic activity for the redn. of H_2O_2. The sensor showed a linear response to H_2O_2 in the concentration range between 7.0 .times. 10-6 and 4.3.times. 10-3 mol L-1 with a high sensitivity, and a detection limit of 2.3 .times. 10-6 mol L-1. Experimental results also showed that the sensor had good stability.

6 Medical and dental

6.1 Carbene complexes of gold: Preparation, medical application and bonding

A review. H Raubenheimer, S Cronje, Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland, S. Africa, *Chemical Society Reviews* 2008, **37(9)**, 1998. New preparative methods for gold carbene complexes have been developed and older ones modified to prepare compounds with specific inherent properties for targeted applications. One of the important areas of application that has grown rapidly and wherein carbene complexes are increasingly significant falls within the field of medicine. Sophisticated theor. calculations have accompanied many synthetic studies. These aspects are covered in this critical review (65 refs.).

6.2 Enhancement of the antitumour activity for the synthesised dodecylcysteine surfactant using gold nanoparticles

In this paper, the surfactant dodecylcysteine hydrochloride was synthesized. The surface parameters of the synthesized surfactant were studied using a surface tension technique. E Azzam, S Morsy, Applied Surfactant Laboratory, Petrochemicals Department, Egyptian, Petroleum Research Institute, Nasr City, Cairo, Egypt, *Journal of Surfactants and Detergents* 2008, **11(3)**, 195. The surface parameters show a good surface activity of the prepared surfactant in aqueous solution. The self-assembling behaviour of the synthesized surfactant comparing with that of cysteine compound on the prepared gold nanoparticles was confirmed using transmission electron microscope (TEM) measurements. The effect of self-assembling of this surfactant on the size of gold nanoparticles was studied using TEM images. The antitumour activity of the prepared surfactant without and with the gold nanoparticles was investigated. The results show that the antitumour activity of the prepared surfactant was enhanced with the presence of the gold nanoparticles.

6.3 A correlation found between gold concentration in blood and patch test reactions in patients with coronary stents

Background: Patients with dental gold restorations are known to have a higher level of gold concentration in blood (B-Au). Objectives: To further investigate, in a study on patients with intracoronary stents and contact allergy to metals, the gold and nickel release from stainless steel stent with (Au stent) and without (Ni stent) gold plating. Method: S Ekqvist, C Svedman, T Lundh, H Moeller, J Bjork, M Bruze, Department of Occupational and Environmental Dermatology, Lund University, Malmoe University Hospital, Malmoe, Sweden, *Contact Dermatitis* 2008, **59(3)**, 137. A total of 460 patients treated with stenting underwent patch testing with metals, and information on gold and nickel exposure and blood samples were collected. About 200 blood samples were randomly selected and the anal. of B-Au and nickel concentration in blood (B-Ni) was made using inductively coupled plasma mass spectrometry. Results: There was a correlation between the intensity of Au patch test reaction and B-Au ($P < 0.001$). This correlation could not be seen between Ni patch test reaction and B-Ni. A Au stent gave a fivefold higher B-Au than a Ni stent. Conclusions: Gold is released from the Au stent and patients with a Au stent have a fivefold higher B-Au than patients with an Ni stent. The patch test reactions for gold were correlated with B-Au.

7 Metallurgy, materials and coatings

7.1 Programmable memory devices using gold nanoparticles capped with alkanethiols of different carbon chain lengths

Electrical bistability is demonstrated in a polymer memory device using polystyrene containing an organic conjugated compd. (8-hydroxyquinoline) and gold nanoparticles (Au NPs) capped with different alkanethiols of carbon chain lengths as the active layer between two metal electrodes. P Lai, J Chen, Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan, *Journal of Vacuum Science & Technology, A: Vacuum, Surfaces, and Films*, 2008, **26(4)**, 1062. Au NPs capped with three different alkanethiols [1-octanethiol (C8), 1-dodecanethiol (C12), and 1-octadecanethiol (C18)] are investigated for the correlation with the memory performance. Above a threshold voltage, the as-fabricated device can transit from low cond. state to high cond. state. By applying a certain positive voltage, the high concentrated state can return to the low concentrated state. The switch-on voltages of thiol-derivatized Au NPs based organic memory devices are almost the same. Current fluctuations appeared in the static current-voltage characteristic of Au NPs capped with a 1-octadecanethiol (C18) based memory device. This feature is related to quantized charging and discharging of Au NPs because of the Coulomb repulsion between electrons confined in nanocrystals.

7.2 Responsive hydrogels with gold nanoparticles as optical sensors

Enhancement of the sensitivity of surface plasmon resonance (SPR) was attempted by assimilating a 2nd plasmon array of Au nanoparticles (Au NPs). J Wackerly, L Thompson, N Rajabali, J Rogers, R Nuzzo, J Moore, Departments of Chemistry and Materials Science & Engineering and the Materials Research Laboratory, University of Illinois at Urbana-Champaign, USA, *PMSE Preprints* 2008, **98**, 105. Varying the size and concn. of the Au NPs in the hydrogel changes the response observed when the analyte solution is altered from basic to acidic. Swelling of the hydrogel produces a more phys. distant Au NPs from one another and the nanostructured surface. The majority of the improvement of the spectroscopic response took place in the visible region. Finally, various cations can be distinguished at the same pH due to their different affinity for the carboxylate anion.

7.3 Temperature effects on the electrical conductivity of thiol encapsulated gold nanoparticle thin films

Presented in this paper are results demonstrating the irreversibility in cond. changes seen for thin, Langmuir-Schaeffer deposited thiol encapsulated gold nanoparticle films raised to a high temperature N Hardy, M Hanwell, T Richardson, Physics and Astronomy, Hicks building,

The University of Sheffield, Sheffield, UK, *Journal of Materials Science: Materials in Electronics*, 2007, **18(9)**, 943. The cond. changes from low values that rapidly increase at higher temp., to values that remain high and are almost linear with temperature. Comparisons are made to the expected behaviour predicted by the conventional model of electron hopping in metal nanoparticle films.

7.4 Microalloying of gold and gold alloys

A review of microalloying of pure gold and gold alloys is presented. Y Ning, Yuantao Kunming Institute of Precious Metals, Kunming, Yunnan, Peop. Rep. China, *Guijinshu* 2008, **29(2)**, 55. The main effects of microalloying elements in gold alloys are hardening, electrical resistance control, grain size refining, and for recrystn. temperature increasing. In nearly all applications, the elements with large difference in m.p. or at. size to gold, and those with low solid soly. in gold, such as alkali- and alkali-earth metals, rare earth metals, high m.p. metals, metalloids, and some simple metals are selected as microalloying elements. Some examples of microalloyed gold alloys are introduced. The effects of many microalloying elements on the properties of gold and gold alloys are often multiple – coincidence. Some selection principles of microalloying elements for gold and gold alloys for various applications are summarized.

8 Nanotechnology

8.1 Microfluidic synthesis and catalytic application of PVP-stabilized, .apprx.1 nm gold clusters

Small poly(N-vinyl-2-pyrrolidone) (PVP)-stabilized Au clusters were prepared by homogeneous mixing of continuous flow feed of aq. AuCl4- and BH4- in a micromixer. H Tsunoyama, N Ichikuni, T Tsukuda, Catalysis Research Center, Hokkaido University, Nishi 10, Kita 21, Sapporo, 001-0021, Japan *Langmuir* 2008, **24(20)**, 11327. Spectroscopic characterization revealed that microfluidic synthesis could yield monodisperse Au:PVP clusters with average diameter of .apprx.1 nm, which is smaller than clusters produced by conventional batch methods. These .apprx.1 nm Au:PVP clusters exhibited higher catalytic activity in aerobic oxidation of p-hydroxybenzyl alc. than did Au:PVP clusters prepared by batch methods.

8.2 "Sweet" gold nanoparticles with oligosaccharide-modified poly(ethyleneimine)

This paper is focused on the use of oligosaccharide-modified hyperbranched poly(ethyleneimines) (PEI) as reducing and stabilizing agent for the formation of gold nanoparticles. A Koeth, J Koetz, D Appelhans, B Voit, Institut fuer Chemie, Universitat Potsdam, Potsdam (Golm), 14476, Germany, *Colloid and Polymer Science* 2008, **286(11)**, 1317. The secondary amino groups of the PEI as linear units are responsible for the reduction process, and the primary amino groups as terminal units are of relevance for the particle stabilization. With regard to the final size and shape of the gold nanoparticles formed, the amount and type (maltose or maltotriose) of oligosaccharide units and structural parameters of the PEI samples are of importance. The smallest particle size of .apprx.2 nm is obtained from a maltose-modified PEI with an excess of linear units. The size and shape of the polymer-stabilized nanoparticles can be further tuned by changing the solute concentration, the time of heating, as well as the pH value.

8.3 Preparation, characterization, and optical properties of gold, silver, and gold-silver alloy nanoshells having silica cores

This report describes the structural and optical properties of a series of spherical shell/core nanoparticles in which the shell is comprised of a thin layer of gold, silver, or gold-silver alloy, and the core is comprised of a monodispersed silica nanoparticle. J Kim, W Bryan, L Randall, Department of Chemistry, University of Houston, Houston, TX, USA, *Langmuir* 2008, **24(19)**, 11147. The silica core particles were prepared using the Stober method, functionalized with terminal amine groups, and then seeded with small gold nanoparticles (.apprx.2 nm in diam.). The gold-seeded silica particles were coated with a layer of gold, silver, or gold-silver alloy via soln.-phase reduction of an appropriate metal ion or mixt. of metal ions.

The size, morphology, and elemental composition of the composite nanoparticles were characterized by field emission SEM (FE-SEM), energy-dispersive x-ray spectroscopy (energy-dispersive x-ray anal.), x-ray diffraction (x-ray diffraction), Fourier transform IR (FT-IR) spectroscopy, thermal gravimetric anal. (TGA), dynamic light scattering (DLS), and TEM. The optical properties of the nanoparticles were analyzed by UV-vis spectroscopy, which showed strong absorptions ranging from 400 nm into the near-IR region, where the position of the plasmon band reflected not only the thickness of the metal shell, but also the nature of the metal comprising the shell. Importantly, the results demonstrate a new strategy for tuning the position of the plasmon resonance without having to vary the core diameter or the shell thickness.

8.4 Polyelectrolyte-mediated non-micellar synthesis of monodispersed aggregates' of gold nanoparticles using a microwave approach

Aggregates of monodispersed gold nanoparticles were prepared in large quantities. Those particles were made in presence or in absence of gold seed in a polyelectrolyte solution using microwave heating for .apprxeq.30-60s. S Kundu, H Liang, Hong, Materials Science and Mechanical Engineering, Texas A&M University, College Station, TX, USA, *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* 2008, **330(2-3)**, 143. The average diameters of the

particles calculated from TEM and SEM anal. were 22 nm. The polyelectrolyte acted as a reducing as well as a stabilizing agent. It controlled the growth of particles by aligning them on the polymeric chain and the nanoparticles were subsequently self-assembled to form an aggregate structure. The procedure is very fast and the particles are stable for at least 6 mo under ambient conditions.

9 Refining

9.1 Electroformed gold from gold mine solutions – a new approach to gold recovery

Lab. and pilot plant investigations aimed at recovering gold as an electroformed sheet from gold eluate and gold leach solns. and slurries are discussed. M Sole, Randburg, 2194, S. Afr., *Publications of the Australasian Institute of Mining and Metallurgy*, 2007, **9/2007** (World Gold 2007), 277. The electrolytic test work undertaken makes use of high surface area electrodes, in particular nickel-chrome foam metal and activated carbon, as well as ultrasonic activation. The process involves initial gold electrowinning (or adsorption onto activated carbon), followed by gold electroforming, both operations being carried out in a specially designed reactor. The pilot plant work mainly involved the treatment of gold eluate solns. from a South African gold mine containing 600 mg/L Au: some tests were also carried out on gold leach solutions containing 6 mg/L Au. In the former case, efficient gold extracton onto the foam metal cathode was achieved using electrolysis combined with ultrasonics.

The polarity of the gold-loaded cathode was then reversed and, using a replacement electroforming electrolyte, gold was electroformed *in situ* onto a polished stainless steel mandrel, from which gold sheet was subsequently removed. In the case of leach solutions, pilot plant tests confirmed lab. findings that in the presence of calcium (resulting from the lime used during the leaching process) no electrowinning is possible. Lab. tests showed, however, that when sodium (in the form of NaOH or Na_2CO_3) is added to the leach solution, electrowinning can indeed take place. Alternatively, if a special activated carbon electrode is used (without current), the non-ionic calcium aurocyanide complex is adsorbed on to the activated carbon. When a gold-loaded activated carbon electrode is made anodic in a gold electroforming electrolyte, gold electroforming is feasible, although the efficiency is low. The possible implications of these developments for gold recovery are further examined.

9.2 A technology of precious metals recovery from gold-bismuth ores

Tests for the development of a metals recovery technol. from samples of a Russian gold-bismuth deposit were carried out. O Khmelnitskaya, V Beskrovnaya, Precious Metals Hydrometallurgy Laboratory, Irgiredmet JSC, Irkutsk, Russia, *Publications of the Australasian Institute of Mining and Metallurgy*, 2007, **9/2007**(World Gold 2007), 245. Gold, silver and bismuth assay reported 5.6 g/t, 3.0 g/t, and 0.08%, resp. Two flow sheet options were pilot plant tested: 1. gravity/cyanidation of gravity tailings with subsequent flotation of cyanidation/carbon-in-pulp (CIP) tailings, and 2. gravity/flotation concn. with cyanidation/CIP of concentrations Option 1 results showed lower gold, silver and bismuth recoveries (81.3% Au, 55% Ag and 74% Bi) due to low flotation efficiency for cyanidation tailings. Therefore, a flow sheet involving gravity/flotation concn. to produce bismuth-gold concentrations. (0.8% Bi) with subsequent cyanidation/CIP was recommended. Gold, silver and bismuth recoveries obtained by this method to the combined gravity/flotation conc. were 90.2% Au, 83.3% Ag and 80.2% Bi of the ore, resp.

Overall gold, silver and bismuth recoveries were 83% Au, 40.5% Ag, and 80.2% Bi, resp. Gold and silver recoveries to the cathode ppt. were 92% Au and 48.6% Ag (per operation). Reagents consumed for flotation were 0.1 kg lead acetate/t ore, 0.4 kg Bu xanthate/t ore, 0.2 kg T-80 frother/t ore, 0.02 kg sodium hexametaphosphate/t ore, 0.15 kg copper sulfate/t ore. Reagents consumption for cyanidation was 0.42-0.48 kg NaCN/t ore and 0.2 kg CaO/t ore. It was recommended to deliver bismuth concentrations after hydrometallurgical treatment to a smelter. Overall bismuth recovery including bismuth recovery achieved by pyrometallurgy was 60.0%. However, delivery of bismuth concentrations to a smelter and their com. treatment would be expensive due to relatively high mass pull of bismuth concentrations (7.6% of the ore wt.). For this reason, thiourea leaching and hydrochloric acid leaching with subsequent cyanidation/CIP were investigated as alternatives to cyanide leaching. These two alternatives were proposed to enable optimal recovery of valuable metals from concentrations on-site. Recoveries obtained by thiourea leaching were 91.2% Au, 90.5-91.9% Bi, and 77-78.1% Ag. However, that method required considerable capital and operating costs. As an alternative, hydrochloric acid leaching with subsequent cyanidation was investigated. Test results showed improved gold, bismuth and silver recoveries, which were 94-95.9% Au, 94-96% Bi, and 76-78% Ag, resp. Hydrochloric acid consumption was 100 kg/t conc. or 7.6 kg/t ore.

Current efficiency during electrowinning was about eight to 12%. A recommended flow sheet involving hydrochloric acid leaching of concs., electrowinning of bismuth from solutions, recycling solutions after electrowinning and cyanidation of hydrochloric acid leaching cakes is described. Overall recoveries achieved by the proposed flow sheet were as follows: 84.8-86.5 Au%, 75.8-76.9 Bi%, and 63.2-64.9 Ag%. Based on results from these tests, initial data for a bankable feasibility study and plant designing were developed.

9.3 Gold in tailings – mineralogical characterization and metallurgical implications

Gold extraction is largely driven by mineralogical factors, which often cause gold losses to various tailings. J Zhou, C Fleming, SGS Lakefield Research Ltd, Lakefield, ON, K0L 2H0, Canada, *Publications of the Australasian Institute of Mining and Metallurgy*, 2007, **9/2007**(World Gold 2007), 311. Mineralogical factors affecting gold recovery include grain size and shape, surface coaling or rimming on gold particles, the presence of cyanide or oxygen-consuming minerals or preg-robbers, the presence of slow-dissolving gold minerals and the refractory nature of submicroscopic gold. Among these factors, locking of fine gold particles in sulfide, silicate and other minerals, either as visible, fine-grained gold inclusions and/or as invisible submicroscopic gold, is by far the most common factor leading to poor gold recovery in gold ore processing. This paper discusses the mineralogical characterization of gold lost in tailings and its metallurgical implications. The techniques used in characterizing the un-recovered gold are also briefly introduced.

9.4 Assessment of options for economic processing of preg-robbin gold ores

One of the challenges facing the gold industry in the 21st century is the continuing need to identify new reserves of economically treatable ores. Discoveries of large, metallurgically simple ore bodies are becoming increasingly rarer, forcing companies to investigate options for the processing of ores which may present recovery, economic and/or environmental issues, requiring innovative approaches to their treatment. Ores which contain naturally occurring carbonaceous material ('preg-robbing ores') are an example of one such ore type. Newmont's Jundee operation contains zones of carbonaceous ore within the oxidized ore body. R Dunne, K Buda, M Hill, W Staunton, V Tjandrawan, G Wardell-Johnson, Newmont Australia, West Perth, WA, Australia, *Publications of the Australasian Institute of Mining and Metallurgy*, 2007, **9/2007**(World Gold 2007), 205. A program consisting of detailed lab. work and extensive plant trials was undertaken to assess the options of the processing of this material. Lab. tests demonstrated the advantage of carbon-in-leach (CIL) over direct cyanide leaching and carbon-in-pulp (CIP) for treatment of these ores. The lab. program identified several factors which would enhance overall gold recoveries where preg-robbing ore was being processed, including: .bul. keeping preg-robbing ore sep. from non-graphitic ore; .bul. maximizing gravity recovery; and .bul. ensuring the plant operates in 'pure' CIL mode, ie no leaching prior to first adsorption tank. Several plant trials were undertaken to assess the economic sustainability of treating moderate preg-robbing ores through a modified gravity/leach/adsorption circuit.

Results indicated that where good operational control of the circuit was maintained to ensure high gravity recovery, minimal leaching prior to carbon contact, and maintenance of good, active carbon inventory, then acceptable and sustainable overall gold recoveries could be obtained. Using these relatively simple plant modifications potentially allows a plant to treat ores with preg-robbing index (PRI) values up to one. When PRI values rise to 1.3-1.6, leach recoveries can drop from >85% to <40%, indicating a more intensive approach may be required, including kerosene addition. and higher carbon inventories and activities.

9.5 Gekko's Gravity, Flotation and Intensive Leaching (GFIL) process for gold recovery improves environmental and cost outcomes

Upward pressure on all mining operations is coming from the triple bottom line. To some extent this is being offset by the rise in mineral prices, but this may or may not continue. S Gray, T Hughes, Gekko Systems Pty Ltd, Ballarat, VIC, 3350, Australia, *Publications of the Australasian Institute of Mining and Metallurgy*, 2007, **9/2007**(World Gold 2007), 229. The other serious issue facing all companies is the replacement of economic reserves as exploration levels over the past decade continued to decline in line with falling mineral prices. In order to underpin the sustainability of the mining industry it is necessary to continue to reduce cost, reduce the mine environmental footprint, while increasing community benefit. At the same time we increase the economic reserves.

The highest risk is in adding new mineral discoveries as the strike rate for economic discovery decreases. Gekko Systems Pty Ltd recognizes that the most simple and risk averse route to increasing economic reserves is to reduce cut-off grade in the mine, thereby bringing formerly uneconomic reserves into the economic category. We were developing a new process flow sheet which embodies the triple bottom line and the issue of economic replacement of reserves. This paper describes this flow sheet and presents four examples where this concept is/can be applied to bring about triple bottom line benefits. Sustainability can only be assured if we are the ones in control of our environment, costs and reserves.

10 General

10.1 Enhanced conversion efficiency in dye-sensitized solar cells based on ZnO bifunctional nanoflowers loaded with gold nanoparticles

The ZnO nanoflowers loaded with gold nanoparticles are synthesized by a hydrothermal method using mixed precursors and controlled conditions. V Dhas, S Muduli, W Lee, S Han, S Ogale, Physical and Materials Chemistry Division, National Chemical Laboratory, Pune, India, *Applied Physics Letters*, 2008, **93(24**), 243108. The dye-sensitized solar cells based on the ZnO nanoflowers with gold

nanoparticles show power conversion efficiency of 2.5%, which is considerably higher than that of ZnO nanoflowers without gold nanoparticles. Detailed characterizations are performed, presented, and discussed. (c) 2008 American Institute of Physics.

10.2 Tone reproduction of gold-layer photograph reversing negative-positive images

Tone of the gold-layer photograph which made images with gold layer using silver salt photog. materials and the gold deposition development was studied. Because the gold-layer absorbs light, it becomes a neg. image by transmitted light, while it is reversed out for the direct pos. image by reflected light because the gold-layer at the high exposure area reflects light strongly. K Kuge, Y Nakanishi, T Sakai, Tomoku, Graduate School of Advanced Integration Science, Chiba University, Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan, *Nippon Shashin Gakkaishi,* 2008, **71(2)**, 86. Both the neg. image and the pos. image appear on the same photograph. The tone reprodn. of those neg. and pos. images was examd. Due to the uniform reflection of gold-layer at highly-exposed areas, the tone at the highlight area got identified, while the transmitted d. for the same area increased with exposure, and a contrasty image was formed.